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Simulation of Edge Effects in Electroanalytical Experiments.
 Part I. Two Dimensional Collocation and Theory for Chronoamperometry.

By
 Bernd Speiser and Stanley Pons
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 in
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University of Alberta
 Department of Chemistry
 Edmonton, Alberta, Canada
 T6G 2G2

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Bernd Speiser and Stanley Pons*		
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The details for accurate simulations of edge effects experienced at disc electrodes in chronoamperometric experiments is given.		

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Simulation of edge-effects in electroanalytical experiments by orthogonal collocation.

Part 1. Two-dimensional collocation and theory for chronoamperometry

BERND SPEISER AND STANLEY PONS

Department of Chemistry, University of Alberta, Edmonton, Alta., Canada T6G 2G2

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A two-dimensional model to describe edge-effects at planar circular disc electrodes has been developed. Two-dimensional orthogonal collocation is used to discretize the corresponding partial differential equations. The equations for the simulation of a chronoamperometric experiment are derived.

BERND SPEISER AND STANLEY PONS: Can. J. Chem. 60, 1352 (1982).

On a mis au point une méthode bidimensionnelle pour décrire les effets d'arête au niveau des électrodes à disques circulaires plans. On a utilisée une discrétisation orthogonale pour les équations différentielles partielles correspondantes. On a dérivé les équations de la simulation d'une expérience de chronoamperométrie.

[Traduit par le journal]

Introduction

One common simplification in the theoretical treatment of electrode processes of planar disc electrodes is the assumption of semi-infinite linear diffusion. This results in the reduction of the three-dimensional system to a one-dimensional model, where the distance x from the electrode surface is the only coordinate to be considered. Consequently, the three-dimensional form of Fick's second law

$$(1) \quad \frac{\partial c}{\partial t} = D \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right]$$

reduces to the simpler differential equation

$$(2) \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

and the mathematical and computational efforts decrease considerably. The assumption of linear diffusion to a planar electrode might imply an infinite disc without edges. For real systems, however, this of course is not possible.

Thus, measurements at finite disc electrodes should deviate from the simple one-dimensional theory. In fact, it has been shown for different electroanalytical techniques such as chronoamperometry and chronopotentiometry (1) that the diffusion current is higher than expected from the theoretical calculations based on eq. [2], i.e. the Cottrell equation (2) for chronoamperometry. For cyclic voltammograms (3) the peak separation is larger than the theoretical values given by Nicholson and Shaw (4). A number of papers have accounted for these deviations as being due to additional diffusion from directions other than perpendicular to the disc electrode (see e.g. refs. 5,

6). In a system with several coupled charge transfer and chemical reactions dramatic changes of the overall voltammogram have been attributed to edge effects (7).

Several attempts have been made to calculate the effects of edge diffusion and to simulate model systems without assuming one-dimensional diffusion (5, 6). Recently, Heinze published a two-dimensional model based on the finite difference method (8, 9), while Oldham (10) and Aoki and Osteryoung (11) developed analytical solutions for the simple reversible mechanism.

These calculations showed, in agreement with experiments, that edge diffusion rates increase with increasing time and decreasing radius of the disc electrode. The deviation from pure Cottrell behavior is claimed to be between 9 and 10% for typical conditions: diffusion coefficient $= 10^{-5} \text{ cm}^2/\text{s}$, electrode radius 0.1 cm, electrolysis time 2.65 s (5, 9-11). All methods presented thus far, however, demonstrate results for only the simplest mechanisms (e.g. reversible electron transfer case). Extensions apparently require extensive computational effort.

Orthogonal collocation has been shown to provide a powerful method to simulate responses of several electroanalytical techniques to a variety of mechanisms (12-18). Up to now all these calculations have been performed using one-dimensional diffusion models. We want to report the construction of a two-dimensional model for the diffusion to and from a planar disc electrode and the discretization of the resulting second order partial differential equations to give a set of simultaneous first order ordinary differential equations.

The comparison of the results of this new model with those already presented is the subject of a

separate report now in preparation. Extensions to other mechanisms and electroanalytical experiments will also be considered.

The two-dimensional model

Consider a planar, circular disc of conducting material imbedded into an insulator (Fig. 1). The radius of the disc is r_0 . The radius r_0 of the insulator may go to infinity. From the symmetry of the problem, it follows that we may use two coordinates x (perpendicular to the disc) and r (along the radius vector of the disc). We are required to calculate the concentration c of all species as a function of x , r and the time t , where c is given by second order partial differential equations of the type (9)

$$(3) \quad \frac{\partial c}{\partial t} = D \left[\frac{\partial^2 c}{\partial x^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right] - f(c)$$

and $f(c)$ is determined by the kinetics of the system investigated. D is the diffusion coefficient.

Let us consider an EC-mechanism (4). There the differential equations describing the concentration of species A, B, and C are given by [5]-[7].

$$(4) \quad A \xrightarrow{-k} B \xrightarrow{-k} C$$

$$(5) \quad \frac{\partial c_A}{\partial t} = D_A \left[\frac{\partial^2 c_A}{\partial x^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} + \frac{\partial^2 c_A}{\partial r^2} \right]$$

$$(6) \quad \frac{\partial c_B}{\partial t} = D_B \left[\frac{\partial^2 c_B}{\partial x^2} + \frac{1}{r} \frac{\partial c_B}{\partial r} + \frac{\partial^2 c_B}{\partial r^2} \right] - k c_A$$

$$(7) \quad \frac{\partial c_C}{\partial t} = D_C \left[\frac{\partial^2 c_C}{\partial x^2} + \frac{1}{r} \frac{\partial c_C}{\partial r} + \frac{\partial^2 c_C}{\partial r^2} \right] + k c_B$$

For $k = 0$ we deal with a simple reversible electron transfer. The electrode reaction is eq. [4] is drawn as an oxidation but the extension to reductions is immediate. For simplification we may assume that the diffusion coefficients are equal:

$$(8) \quad D_A = D_B = D_C$$

This, however, is not necessary for orthogonal collocation simulations.

Depending on the electroanalytical method we wish to simulate for the mechanism chosen, certain initial and boundary conditions are imposed upon the solution of eq. [3]. Let us consider a chronoamperometric experiment, where species A, the substrate, is present at a homogeneous concentration c_A^0 at the beginning of the experiment. The product

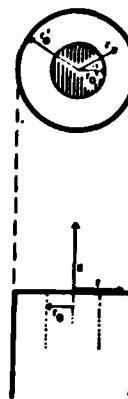


FIG. 1. Geometry of the two-dimensional model.

species B and C may not be present at $t = 0$ (initial conditions [9], [10]).

$t = 0, x \geq 0, r \geq 0$

[9] $c_A(x, r, 0) = c_A^0$

[10] $c_B(x, r, 0) = c_C(x, r, 0) = 0$

At the boundary $x \rightarrow \infty$, i.e. at a distance x from the electrode where the concentrations are not changed during the experiment:

$t > 0, x \rightarrow \infty, r \geq 0$

[11] $c_A(\infty, r, t) = c_A^0$

[12] $c_B(\infty, r, t) = c_C(\infty, r, t) = 0$

The same condition may hold for a distance r from the electrode radially:

$t > 0, x \geq 0, r \rightarrow \infty$

[13] $c_A(x, \infty, t) = c_A^0$

[14] $c_B(x, \infty, t) = c_C(x, \infty, t) = 0$

At the electrode surface the Nernst equation has to be fulfilled for c_A and c_B (eq. [14a]). If we step to a potential E at least 200 mV past the formal potential $E_{1/2}$, the concentration of the substrate A at the electrode is immediately forced to zero and [14a] may be replaced by [14b]. Additional conditions at

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the electrode surface are given by the flux equations [15] and [16].

$$(14a) \quad i > 0, x = 0, 0 \leq r \leq r_0$$

$$(14a) \quad \frac{c_A(0, r, t)}{c_B(0, r, t)} = \exp \left[\frac{nF}{RT} (E^\circ - E) \right]$$

$$(14b) \quad c_A(0, r, t) = 0$$

$$(15) \quad \left(\frac{\partial c_A}{\partial r} \right)_{r=0} = - \left(\frac{\partial c_B}{\partial r} \right)_{r=0}$$

$$(16) \quad \left(\frac{\partial c_C}{\partial r} \right)_{r=0} = 0$$

At $x = 0$, but outside the electroactive area ($r > r_0$), no species may undergo electron transfer and we have boundary condition [17].

$$i > 0, x = 0, r_0 \leq r \rightarrow \infty$$

$$(17) \quad \left(\frac{\partial c_A}{\partial r} \right)_{r \rightarrow \infty} = \left(\frac{\partial c_B}{\partial r} \right)_{r \rightarrow \infty} = \left(\frac{\partial c_C}{\partial r} \right)_{r \rightarrow \infty} = 0$$

Because of the symmetry of the problem there may be no net flux of any species across the x -axis at the center of the electrode ($r = 0$).

$$i > 0, x \geq 0, r = 0$$

$$(18) \quad \left(\frac{\partial c_A}{\partial r} \right)_{r=0} = \left(\frac{\partial c_B}{\partial r} \right)_{r=0} = \left(\frac{\partial c_C}{\partial r} \right)_{r=0} = 0$$

Equations [4]–[8] describe the two-dimensional model system for an EC-mechanism under chronoamperometric conditions.

Since there are different boundary conditions for $x = 0$ inside ($r \leq r_0$) and outside ($r > r_0$) the electrode, it is convenient to describe the whole system by two concentration functions c_1 and c_2 which are defined for $0 \leq r \leq r_0$ and $r_0 < r$ respectively. To avoid discontinuities at $r = r_0$ we have to apply some additional "boundary" conditions for all species:

$$(19) \quad c_1(x, r_0, t) = c_2(x, r_0, t)$$

The second derivative of c with respect to r is only defined if the first derivative with respect to r has no discontinuity at $r = r_0$ and this gives the further conditions

$$(20) \quad \left(\frac{\partial c_1}{\partial r} \right)_{r_0} = \left(\frac{\partial c_2}{\partial r} \right)_{r_0}$$

for all species.

It has been pointed out (12) that orthogonal collocation may be applied only to dimensionless systems which have been converted from semi-infinite models to models in the range 0 to 1.

In order to meet these requirements we use the following transformation equations:

$$(21) \quad X = x/L$$

$$(22) \quad c^* = c/L$$

$$(23a) \quad R = r/r_0$$

$$(23b) \quad R' = (r - r_0)/(M - r_0)$$

$$(24) \quad u = k \cdot r / D$$

$$(25) \quad T' = D t / \delta t$$

where X is the dimensionless distance from the electrode, L is the distance from the electrode in the x direction defined so that at $X = L$ no changes in concentration take place during the time of the experiment, c^* is the dimensionless concentration, R and R' are the dimensionless distances in the r direction inside and outside the electrode disc respectively, M is the distance in the r direction defined in the same manner as L , and T' is the dimensionless simulation time.

Application of eqs. [21]–[25] and the subdivision into inner and outer functions c_1 and c_2 of eqs. [4]–[8] yield the dimensionless model [26]–[33].

$$(26) \quad \frac{\partial c_{1A}}{\partial T'} = \beta \frac{\partial^2 c_{1A}}{\partial X^2} + \frac{1}{R} \frac{\partial c_{1A}}{\partial R} + \frac{\partial^2 c_{1A}}{\partial R'^2} - u c_{1B}$$

$$(27) \quad \frac{\partial c_{1B}}{\partial T'} = \beta \frac{\partial^2 c_{1B}}{\partial X^2} + \frac{1}{R} \frac{\partial c_{1B}}{\partial R} + \frac{\partial^2 c_{1B}}{\partial R'^2} - u c_{1A}$$

$$(28) \quad \frac{\partial c_{1C}}{\partial T'} = \beta \frac{\partial^2 c_{1C}}{\partial X^2} + \frac{1}{R} \frac{\partial c_{1C}}{\partial R} + \frac{\partial^2 c_{1C}}{\partial R'^2} + u c_{1B}$$

where

$$(29) \quad \beta = r_0 / L^2$$

and

$$(30) \quad \frac{\partial c_{2A}}{\partial T'} = \beta \frac{\partial^2 c_{2A}}{\partial X^2} + \frac{\beta'}{R' + \sqrt{\beta'}} \frac{\partial c_{2A}}{\partial R'} + \beta' \frac{\partial^2 c_{2A}}{\partial R'^2}$$

$$(31) \quad \frac{\partial c_{2B}}{\partial T'} = \beta \frac{\partial^2 c_{2B}}{\partial X^2} + \frac{\beta'}{R' + \sqrt{\beta'}} \frac{\partial c_{2B}}{\partial R'} + \beta' \frac{\partial^2 c_{2B}}{\partial R'^2} - u c_{2A}$$

$$(32) \quad \frac{\partial c_{2C}}{\partial T'} = \beta \frac{\partial^2 c_{2C}}{\partial X^2} + \frac{\beta'}{R' + \sqrt{\beta'}} \frac{\partial c_{2C}}{\partial R'} + \beta' \frac{\partial^2 c_{2C}}{\partial R'^2} + u c_{2B}$$

in order to meet these requirements we use the following transformation equations:

where

$$(33) \quad \beta' = r_0 / (M - r_0)$$

with the initial conditions

$$T' = 0, 0 \leq X \leq 1, 0 \leq R \leq 1, 0 \leq R' \leq 1$$

$$(34) \quad c_{1A}(X, R, 0) = c_{2A}(X, R', 0) = 1$$

$$(35) \quad c_{1B}(X, R, 0) = c_{2B}(X, R', 0) = c_{1C}(X, R, 0) = c_{2C}(X, R', 0) = 0$$

and boundary conditions

$$T' > 0, X = 0, 0 \leq R \leq 1$$

$$(36) \quad c_{1A}(1, R, T') = 1$$

$$(37) \quad c_{1B}(1, R, T') = c_{1C}(1, R, T') = 0$$

$$T' > 0, X = 1, 0 \leq R \leq 1$$

$$(38) \quad c_{2A}(1, R', T') = 1$$

$$(39) \quad c_{2B}(1, R', T') = c_{2C}(1, R', T') = 0$$

$$T' > 0, X \leq 1, R = 1$$

$$(40) \quad c_{1A}(X, 1, T') = 1$$

$$(41) \quad c_{1B}(X, 1, T') = c_{2A}(X, 1, T') = 0$$

$$T' > 0, X = 0, 0 \leq R \leq 1$$

$$(42a) \quad c_{1A}(0, R, T') = \exp \left[\frac{nF}{RT} (E^\circ - E) \right]$$

$$(42b) \quad c_{1B}(0, R, T') = 0$$

$$(43) \quad \left(\frac{\partial c_{1A}}{\partial R} \right)_{r=0} = - \left(\frac{\partial c_{1B}}{\partial R} \right)_{r=0}$$

$$(44) \quad \left(\frac{\partial c_{1C}}{\partial R} \right)_{r=0} = 0$$

$$T' > 0, X = 0, 0 \leq R' \leq 1$$

$$(45) \quad \left(\frac{\partial c_{1A}}{\partial R'} \right)_{r=0} = \left(\frac{\partial c_{1B}}{\partial R'} \right)_{r=0} = \left(\frac{\partial c_{1C}}{\partial R'} \right)_{r=0} = 0$$

$$T' > 0, 0 \leq X \leq 1, R = 0$$

$$(46) \quad \left(\frac{\partial c_{1A}}{\partial R} \right)_{r=0} = \left(\frac{\partial c_{1B}}{\partial R} \right)_{r=0} = \left(\frac{\partial c_{1C}}{\partial R} \right)_{r=0} = 0$$

$$T' > 0, 0 \leq X \leq 1, R = 1 (R' = 0)$$

$$(47) \quad c_{1A}(X, 1, T') = c_{1B}(X, 0, T')$$

$$(48) \quad c_{1A}(X, 1, T') = c_{1B}(X, 0, T')$$

$$(49) \quad c_{1A}(X, 1, T') = c_{1C}(X, 0, T')$$

$$(50) \quad \left(\frac{\partial c_{1A}}{\partial R'} \right)_{r=0} = - \sqrt{\beta'} \left(\frac{\partial c_{1A}}{\partial R'} \right)_{r=0}$$

$$(51) \quad \left(\frac{\partial c_{1B}}{\partial R'} \right)_{r=0} = - \sqrt{\beta'} \left(\frac{\partial c_{1B}}{\partial R'} \right)_{r=0}$$

$$(52) \quad \left(\frac{\partial c_{1C}}{\partial R'} \right)_{r=0} = \sqrt{\beta'} \left(\frac{\partial c_{1C}}{\partial R'} \right)_{r=0}$$

We have to calculate the inner and outer concentrations of species A, B, and C respectively as a function of X , $R(R')$, and T' .

Two-dimensional collocation

Orthogonal collocation uses a mathematically suitable trial function to describe the solution of a differential equation at certain points. If one uses a set of weighted orthogonal polynomials as the trial function, the differential equation is satisfied at the zeroes of the polynomial of highest order used (19, 20) for a set of coefficients which depend on time.

To perform orthogonal collocation in two-dimensions, x and r , we use a trial function depending on x and r

$$(53) \quad c(x, r, t) = \lambda_{11} x^{n_1} r^{n_2} + \lambda_{12} x^{n_1} r^{n_3} + \dots + \lambda_{1N_1} x^{n_1} r^{n_{N_1}} + \lambda_{21} x^{n_2} r^{n_1} + \lambda_{22} x^{n_2} r^{n_3} + \dots + \lambda_{2N_2} x^{n_2} r^{n_{N_2}} + \dots + \lambda_{N_1 N_2} x^{n_{N_1}} r^{n_{N_2}}$$

or

$$(54) \quad c(x, r, t) = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \lambda_{ij} x^{n_i} r^{n_j}$$

i.e. we represent the concentration by a polynomial in x and r whose time-dependent coefficients are the λ_{ij} . The polynomial is of order $N_1 + 2$ and $N_2 + 2$ with respect to x and r , respectively. The

dummy variables j and i perform the summations over the powers of x and r respectively.

The coefficients are determined then, that at all collocation points (x_i, r_j) , i.e. $N_1 + 2$ and $N_2 + 2$

points in the x and r directions, respectively

$$(55) \quad c(x_i, r_j, t) = \sum_{i=1}^{n+1} \sum_{j=1}^{n+1} \lambda_{i,j} s_i^{-1} r_j^{-1}$$

The concentrations at the collocation points may be the elements of a concentration matrix $\Gamma_{1,0}$

$$(56) \quad \Gamma_{1,0} = X_{1,0} \cdot A_{1,0} \cdot R_{1,0}^T$$

which is calculated by multiplication of a matrix $X_{1,0}$, containing the s_i^{-1} as elements, a matrix $A_{1,0}$, containing the elements $\lambda_{i,j}$, and a matrix $R_{1,0}^T$, containing the elements r_j^{-1} . The superscript T denotes a transposed matrix.

Now we can calculate the first and second derivatives of the concentration at the collocation points with respect to x and r respectively:

$$(57) \quad \Gamma_{1,1}' = X_{1,1} \cdot A_{1,1} \cdot R_{1,1}^T$$

$$(58) \quad \Gamma_{1,2}'' = X_{1,2} \cdot A_{1,2} \cdot R_{1,2}^T$$

$$(59) \quad \Gamma_{1,3}''' = X_{1,3} \cdot A_{1,3} \cdot R_{1,3}^T$$

$$(60) \quad \Gamma_{1,4}'''' = X_{1,4} \cdot A_{1,4} \cdot R_{1,4}^T$$

where the superscript $s_i(r)$ denotes the first and accordingly $s_i'(r)$ characterizes the second derivative with respect to r .

From eq. [56] it follows that

$$(61) \quad A_{1,1} = X_{1,1} \cdot \Gamma_{1,0} \cdot (\Gamma_{1,0}^T)^{-1}$$

After inserting [61] into [57] we arrive at

$$(62) \quad \Gamma_{1,1}' = X_{1,1} \cdot X_{1,0} \cdot \Gamma_{1,0}$$

where the first derivative of the concentration with respect to x is expressed as a function of the concentration itself. In analogy eqs. [61] and [58] give

$$(63) \quad \Gamma_{1,2}'' = X_{1,2} \cdot X_{1,0} \cdot \Gamma_{1,0} = B_{1,2} \cdot \Gamma_{1,0}$$

From [61] and [59] we get

$$(64) \quad \Gamma_{1,3}''' = \Gamma_{1,3} \cdot (B_{1,3} \cdot R_{1,3})^{-1} \cdot B_{1,3}''' = \Gamma_{1,3} \cdot (R_{1,3})^2 \cdot R_{1,3}''' = \Gamma_{1,3} \cdot (R_{1,3} \cdot R_{1,3})^2$$

or

$$(65) \quad \Gamma_{1,3}''' = \Gamma_{1,3} \cdot C_{1,3}$$

Analogous from [61] and [60]

$$(66) \quad \Gamma_{1,4}'''' = \Gamma_{1,4} \cdot (B_{1,4} \cdot R_{1,4})^{-1} \cdot B_{1,4}'''' = \Gamma_{1,4} \cdot B_{1,4}$$

We now calculate the matrices containing the derivatives of the concentration at the collocation points from the concentration matrix once the matrices $A_{1,0}$, $B_{1,1}$, $C_{1,2}$, and $D_{1,3}$ have been determined. Returning to summation expressions we

can write

$$(67) \quad \left(\frac{\partial c}{\partial x} \right)_{x_i, r_j} = \sum_{i=1}^{n+1} A_{1,i} c(x_i, r_j, t)$$

$$(68) \quad \left(\frac{\partial^2 c}{\partial x^2} \right)_{x_i, r_j} = \sum_{i=1}^{n+1} B_{1,i} c(x_i, r_j, t)$$

$$(69) \quad \left(\frac{\partial c}{\partial r} \right)_{x_i, r_j} = \sum_{i=1}^{n+1} C_{1,i} c(x_i, r_j, t)$$

and

$$(70) \quad \left(\frac{\partial^2 c}{\partial r^2} \right)_{x_i, r_j} = \sum_{i=1}^{n+1} D_{1,i} c(x_i, r_j, t)$$

As has been pointed out by Whiting and Carr (12) for the one-dimensional case, the matrices $A_{1,0}$, $B_{1,1}$, $C_{1,2}$, and $D_{1,3}$ depend solely on the type of polynomial used as trial function and may be calculated from the zeroes of the polynomial. This has to be done only once. Using the values of the elements of these matrices we are able to express the differential quotients of c with respect to x and r at all collocation points.

For linear diffusion problems it has been shown that Legendre polynomials are most suitable (12). Pons (18) used Chebyshev polynomials for diffusion under spherical geometry. It may be noted, however, that the choice of the trial function does not have a large effect on the accuracy of the solutions for higher order approximations. In general, the best trial function is determined by the symmetry of the problem.

In this work, Legendre polynomials have been used for discretization along the x -coordinate. The collocation in the direction of the r -coordinate has been performed using different types of functions including Legendre, Chebyshev, and polynomials constructed from even powers of r , which is suggested by the symmetry of the problem around $r = 0$ (19).

Discretization of the equations for chromatoperometry

We can substitute the summation expressions [67]–[70] for the partial differential quotients in eqs. [26]–[28] and [30]–[32]. This yields expressions for the time derivative of the concentration of species A, B, and C at all the collocation points as a function of the concentrations at the collocation points. If we substitute the boundary conditions [36]–[41], [42a] (i.e. we assume a step to a potential far behind E^0) and [47]–[49], we arrive at

$$(71) \quad \left. \frac{dc_1}{dt} \right|_{x_i, r_j} = \beta \cdot \left[B_{1,1} c_1 + \sum_{i=1}^{n+1} B_{1,i} c_1(x_i, R_0, T) \right] + \left[E_{1,1} c_1(X_1, 0, T) + E_{1,n+1} c_1(X_1, 1, T) + \sum_{i=1}^{n+1} E_{1,i} c_1(X_1, R_0, T) \right]$$

$$(72) \quad \left. \frac{dc_2}{dt} \right|_{x_i, r_j} = \beta \cdot \left[B_{1,2} c_2 + \sum_{i=1}^{n+1} B_{1,i} c_2(x_i, R_0, T) \right] + \left[E_{1,2} c_2(X_1, 0, T) + E_{1,n+2} c_2(X_1, 1, T) + \sum_{i=1}^{n+1} E_{1,i} c_2(X_1, R_0, T) \right] - u c_2$$

$$(73) \quad \left. \frac{dc_3}{dt} \right|_{x_i, r_j} = \beta \cdot \left[B_{1,3} c_3 + \sum_{i=1}^{n+1} B_{1,i} c_3(x_i, R_0, T) \right] + \left[E_{1,3} c_3(X_1, 0, T) + E_{1,n+3} c_3(X_1, 1, T) + \sum_{i=1}^{n+1} E_{1,i} c_3(X_1, R_0, T) \right] + u c_3$$

$$(74) \quad \left. \frac{dc_1}{dt} \right|_{x_i, R_0} = \beta \cdot \left[B_{1,1} c_1(X_1, 0, R_0, T) + B_{1,n+1} c_1(X_1, R_0, T) \right] + \left[F_{1,1} c_1(X_1, 0, T) + F_{1,n+1} c_1(X_1, R_0, T) \right] + \beta' \left[F_{1,1} c_1(X_1, 0, T) + F_{1,n+1} c_1(X_1, R_0, T) \right]$$

$$(75) \quad \left. \frac{dc_2}{dt} \right|_{x_i, R_0} = \beta \cdot \left[B_{1,2} c_2(X_1, 0, R_0, T) + \sum_{i=1}^{n+1} B_{1,i} c_2(X_1, R_0, T) \right] + \beta \left[F_{1,2} c_2(X_1, 0, T) + \sum_{i=1}^{n+1} F_{1,i} c_2(X_1, R_0, T) \right] - u c_2$$

$$(76) \quad \left. \frac{dc_3}{dt} \right|_{x_i, R_0} = \beta \cdot \left[B_{1,3} c_3(X_1, 0, R_0, T) + \sum_{i=1}^{n+1} B_{1,i} c_3(X_1, R_0, T) \right] + \beta \left[F_{1,3} c_3(X_1, 0, T) + \sum_{i=1}^{n+1} F_{1,i} c_3(X_1, R_0, T) \right] + u c_3$$

where

$$(77) \quad E_{1,i} = \frac{C_{1,i} + R_0 D_{1,i}}{R_0}$$

and

$$(78) \quad F_{1,i} = \frac{C_{1,i}}{\sqrt{\beta^2 + R_0^2}} + D_{1,i}$$

The primed terms, except T' and B' , correspond to the outer functions. Equations [71]–[76] contain $9N_r + 2N_b + 3N_c$ unknowns, i.e. $c_1(X_1, 0, T)$, $c_1(X_1, 1, T)$, $c_2(X_1, 0, T)$, $c_2(X_1, 1, T)$, $c_3(X_1, 0, T)$, $c_3(X_1, 1, T)$, $c_1(X_1, 0, R_0, T)$, $c_1(X_1, R_0, T)$ and $c_2(X_1, 0, R_0, T)$ for all R_0 ; $c_1(X_1, 0, T')$, $c_1(X_1, R_0, T')$, $c_2(X_1, 0, T')$, $c_2(X_1, R_0, T')$ for all R_0' which may be computed from the boundary conditions as is shown below.

Condition [43] yields

$$(79) \quad \sum_{i=1}^{n+1} A_{1,i} c_1(X_1, R_0, T) = - \sum_{i=1}^{n+1} A_{1,i} c_1(X_1, R_0, T')$$

Expanding the sums, introducing [36], [37], and [42a], and solving for the concentration of species B at the electrode surface ($X_1 = 0$) gives:

$$(80) \quad c_A(0, R_0, T) = -\frac{1}{A_{1,1}} \left[A_{1,n+1} + \sum_{i=1}^{n-1} A_{i,1} c_A(X_i, R_0, T) + c_A(X_n, R_0, T) \right]$$

Condition (44) is changed to

$$\sum_{i=1}^{n-1} A_{i,1} c_A(X_i, R_0, T) = 0$$

which gives, after introduction of (37),

$$(81) \quad c_A(0, R_0, T) = -\frac{1}{A_{1,1}} \sum_{i=1}^{n-1} A_{i,1} c_A(X_i, R_0, T)$$

In analogy it may be derived from (45) and (49) or (41)

$$(82) \quad c_B(0, R_0, T) = -\frac{1}{A_{1,1}} \left[A_{1,n+1} + \sum_{i=1}^{n-1} A_{i,1} c_B(X_i, R_0, T) \right]$$

$$(83) \quad c_C(0, R_0, T) = -\frac{1}{A_{1,1}} \sum_{i=1}^{n-1} A_{i,1} c_C(X_i, R_0, T)$$

and

$$(84) \quad c_D(0, R_0, T) = -\frac{1}{A_{1,1}} \sum_{i=1}^{n-1} A_{i,1} c_D(X_i, R_0, T)$$

The condition (46) gives, for species A, B, and C

$$(85) \quad c_A(X_0, 0, T) = -\frac{1}{C_{1,1}} \left[C_{n+1,1} c_A(X_0, 1, T) + \sum_{i=1}^{n-1} C_{i,1} c_A(X_i, R_0, T) \right]$$

$$(86) \quad c_B(X_0, 0, T) = -\frac{1}{C_{1,1}} \left[C_{n+1,1} c_B(X_0, 1, T) + \sum_{i=1}^{n-1} C_{i,1} c_B(X_i, R_0, T) \right]$$

and

$$(87) \quad c_C(X_0, 0, T) = -\frac{1}{C_{1,1}} \left[C_{n+1,1} c_C(X_0, 1, T) + \sum_{i=1}^{n-1} C_{i,1} c_C(X_i, R_0, T) \right]$$

Condition (50) yields

$$(88) \quad \sum_{i=1}^{n-1} C_{i,1} c_A(X_i, R_0, T) = \sum_{i=1}^{n-1} \sqrt{P} C_{i,1} c_A(X_i, R_0, T)$$

which may be expanded and transformed using (40) and (47)

$$(89) \quad [c_{n+1,n+1} - \sqrt{P} C_{1,1}] c_A(X_0, 1, T) + c_{1,n+1} c_A(X_0, 0, T) \\ = - \sum_{i=1}^{n-1} C_{i,1} c_A(X_i, R_0, T) + \sum_{i=1}^{n-1} \sqrt{P} C_{i,1} c_A(X_i, R_0, T) + \sqrt{P} C_{n+1,1}$$

From (85) and (89) it follows that

$$(90) \quad c_A(X_0, 1, T) = c_A(X_0, 0, T) = -\frac{1}{G_1} \left[\sum_{i=1}^{n-1} A_{i,1} c_A(X_i, R_0, T) + \sum_{i=1}^{n-1} C_{i,1} \sqrt{P} C_{i,1} c_A(X_i, R_0, T) + C_{1,1} \sqrt{P} C_{n+1,1} \right]$$

where

$$(91) \quad G_1 = [C_{n+1,n+1} - \sqrt{P} C_{1,1}] C_{1,1} - C_{1,n+1} C_{n+1,1}$$

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and

$$(92) \quad H_1 = C_{1,n+1} C_{1,1} - C_{1,1} C_{n+1,1}$$

Conditions (46) and (51) ((46) and (52)) are treated similarly using the corresponding boundary conditions. Thus,

$$(93) \quad c_A(X_0, 1, T) = c_A(X_0, 0, T) = -\frac{1}{G_1} \left[\sum_{i=1}^{n-1} H_i c_A(X_i, R_0, T) + \sum_{i=1}^{n-1} C_{i,1} \sqrt{P} C_{i,1} c_A(X_i, R_0, T) \right]$$

and

$$(94) \quad c_B(X_0, 1, T) = c_B(X_0, 0, T) = -\frac{1}{G_1} \left[\sum_{i=1}^{n-1} H_i c_B(X_i, R_0, T) + \sum_{i=1}^{n-1} C_{i,1} \sqrt{P} C_{i,1} c_B(X_i, R_0, T) \right]$$

Finally, the concentrations of species A at $R = 0$ and all X_i may be calculated by introducing (90) into (85):

$$(95) \quad c_A(X_i, 0, T) = -\frac{1}{G_1} \left[\sum_{j=1}^{n-1} G_j c_A(X_j, R_0, T) + \sum_{j=1}^{n-1} C_{j,1} \sqrt{P} C_{j,1} c_A(X_j, R_0, T) + C_{1,n+1} \sqrt{P} C_{n+1,1} \right]$$

while it holds from (93) and (96) (94) and (97), that

$$(96) \quad c_B(X_i, 0, T) = -\frac{1}{G_1} \left[\sum_{j=1}^{n-1} G_j c_B(X_j, R_0, T) + \sum_{j=1}^{n-1} C_{j,1} \sqrt{P} C_{j,1} c_B(X_j, R_0, T) \right]$$

and that

$$(97) \quad c_C(X_i, 0, T) = -\frac{1}{G_1} \left[\sum_{j=1}^{n-1} G_j c_C(X_j, R_0, T) + \sum_{j=1}^{n-1} C_{j,1} \sqrt{P} C_{j,1} c_C(X_j, R_0, T) \right]$$

Now we may substitute the unknown terms in eqs. (71)-(76). From (71), using (90) and (95) it follows

$$(98) \quad \frac{dc_A}{dT} \Big|_{R=0} = -\frac{1}{G_1} \left[E_{1,n+1} + \sum_{i=1}^{n-1} E_{i,1} c_A(X_i, R_0, T) \right] + \frac{1}{G_1} \left[I_{1,1} \sqrt{P} C_{1,1} \right. \\ \left. + \sum_{i=1}^{n-1} [I_{i,1} (\sqrt{P} C_{i,1} - C_{i,n+1}) - I_{1,1} C_{i,n+1} + I_{1,1} C_{1,n+1} c_A(X_i, R_0, T)] \right. \\ \left. + \sum_{i=1}^{n-1} I_{1,1} \sqrt{P} C_{i,1} c_A(X_i, R_0, T) \right]$$

where

$$(99) \quad I_{1,1} = E_{n+1,n+1} C_{1,1} - E_{1,1} C_{n+1,1}$$

and

$$(100) \quad I_{i,1} = E_{i,n+1} C_{1,1} - E_{1,1} C_{i,n+1}$$

Combination of (72) with (98), (93), and (96) gives

$$(101) \quad \frac{dc_A}{dT} \Big|_{R=0} = -\frac{1}{G_1} \left[\sum_{i=1}^{n-1} E_{i,1} c_A(X_i, R_0, T) - E_{1,1} \left[A_{1,n+1} + \sum_{i=1}^{n-1} A_{i,1} c_A(X_i, R_0, T) \right] \right] \\ + \frac{1}{G_1} \left[\sum_{i=1}^{n-1} [I_{i,1} (\sqrt{P} C_{i,1} - C_{i,n+1}) - I_{1,1} C_{i,n+1} + I_{1,1} C_{1,n+1} c_A(X_i, R_0, T)] \right. \\ \left. + \sum_{i=1}^{n-1} I_{1,1} \sqrt{P} C_{i,1} c_A(X_i, R_0, T) \right] - \text{etc.}$$

where

$$(102) \quad K_{1,0} = B_{1,0}A_{1,1} - B_{1,1}A_{1,0}$$

For the inner function describing the concentration of species C it holds from [73] with [81], [94] and [97]

$$(103) \quad \begin{aligned} \frac{dc_1}{dt} \Big|_{R=R_i} = & \frac{\beta}{A_{1,1}} \left[\sum_{j=1}^{n+1} K_{1,j} c_1(X_j, R_i, T) \right] \\ & + \frac{1}{G_1} \left[\sum_{j=1}^{n+1} I_{1,j} (\sqrt{D} C_{1,j} - C_{1,j+1,n+2}) - I_{1,0} C_{1,n+2} + I_{1,n} C_{1,n+2} k_{1,2}(X_n, R_i, T) \right] \\ & + \sum_{j=1}^{n+1} I_{1,j} \sqrt{D} C_{1,j} c_1(X_j, R_i, T) \Big] + ac_1 \end{aligned}$$

The outer functions for all three species are derived following the same scheme. The time derivative of c_1 in the outer domain is found from [74], [82], and [90], and in analogy the corresponding equations for species B or C may be calculated from [75], [83], and [93] or [76], [84], and [94].

$$(104) \quad \begin{aligned} \frac{dc_1}{dt} \Big|_{R=R_o} = & \frac{\beta}{A_{1,1}} \left[K_{1,n+2} + \sum_{j=1}^{n+1} K_{1,j} c_1(X_j, R_o, T) \right] \\ & + \frac{\beta'}{G_1} \left[L_{1,n+2} + \sum_{j=1}^{n+1} F_{1,j} N_j c_1(X_j, R_o, T) + \sum_{j=1}^{n+1} L_{1,j} c_1(X_j, R_o, T) \right] \end{aligned}$$

with

$$(105) \quad L_{1,0} = F_{1,0} G_1 + C_{1,0} \sqrt{D} C_{1,1} F_{1,0}$$

$$(106) \quad \begin{aligned} \frac{dc_1}{dt} \Big|_{R=R_o} = & \frac{\beta}{A_{1,1}} \left[\sum_{j=1}^{n+1} K_{1,j} c_1(X_j, R_o, T) \right] \\ & + \frac{\beta'}{G_1} \left[\sum_{j=1}^{n+1} F_{1,j} N_j c_1(X_j, R_o, T) + \sum_{j=1}^{n+1} L_{1,j} c_1(X_j, R_o, T) \right] - ac_1 \end{aligned}$$

$$(107) \quad \begin{aligned} \frac{dc_1}{dt} \Big|_{R=R_i} = & \frac{\beta}{A_{1,1}} \left[\sum_{j=1}^{n+1} K_{1,j} c_1(X_j, R_i, T) \right] \\ & + \frac{\beta'}{G_1} \left[\sum_{j=1}^{n+1} F_{1,j} N_j c_1(X_j, R_i, T) + \sum_{j=1}^{n+1} L_{1,j} c_1(X_j, R_i, T) \right] + ac_1 \end{aligned}$$

Now the set of six second order partial differential equations [26]–[28] and [30]–[32] has been transformed into a set of $3N_f(N_o + N_i)$ simultaneous ordinary differential equations [98], [101], [103], [104], [106], and [107]. Such systems may be easily integrated by computer programs to give the time dependence of the concentrations of species A, B, and C at the collocation points (X_i, R_i) and (X_o, R_o) . We describe the concentration profiles which develop in front of the electrode by the concentrations at the collocation points.

We note the structural similarity of the formulas describing the time derivatives of the concentrations. This is one of the advantages of the orthogonal

collocation method, for if the theory has been derived once it is very easy to express it in a computer language. Furthermore, if more complicated mechanisms are to be simulated, only minor changes in the formulae have to be performed. Also, the extension of the theory to other experimental techniques, i.e. other boundary conditions, is easy. This will be shown in another paper of this series.

We also note that the implementation of the expressions describing species C is not essential to calculate the concentration profiles of A and B, for C is not electroactive and does not react to or with an electroactive intermediate (16). However, if one

desires, for example, to calculate the spectroelectrochemical response (14) of species C one is interested in the concentration profiles of C as well.

Calculation of the current

In the one-dimensional diffusion model the current i is simply calculated from the flux of the substrate at the electrode surface:

$$(108) \quad i = nFAD \left(\frac{\partial c_A}{\partial x} \right)_{x=0}$$

where A is the electroactive area of the electrode. This implies that the flux of the substrate is uniform over A .

This is clearly not true in the case of a two-dimensional model considering edge effects. Instead, the current is given by

$$(109) \quad i = nFD \int_0^r 2\pi r \left(\frac{\partial c_A}{\partial x} \right)_{x=0} dr$$

where the r -dependent flux through an infinitesimally small part $2\pi r dr$ of the electrode is integrated over the electroactive section $0-r_0$ of the r -coordinate.

Using the transformation equations [21]–[23], [25], and the definition of β (eq. [29]), eq. (109) yields

$$(110) \quad i = \frac{nFD\pi r_0 k_A}{L} \int_0^r R \left(\frac{\partial c_1}{\partial X} \right)_{x=0} dR = \sum_{j=1}^{n+1} Q_j$$

$$= 2nFAd_1 \frac{\sqrt{D}}{\sqrt{t}} \sqrt{\beta T} \int_0^r R \left(\frac{\partial c_1}{\partial X} \right)_{x=0} dR$$

The chronocomperometric "constant" $1/\sqrt{i}$ is given by

$$(111) \quad 1/\sqrt{i} = 2nFAd_1 \frac{\sqrt{D}}{\sqrt{t}} \sqrt{\beta T} \int_0^r R \left(\frac{\partial c_1}{\partial X} \right)_{x=0} dR$$

Alternatively, we may express this product in terms of the "Cottrell constant" (2)

$$(112) \quad (1/\sqrt{i})_c = \frac{nFAd_1 \sqrt{D}}{\sqrt{t}}$$

or

$$(113) \quad \frac{1/\sqrt{i}}{(1/\sqrt{i})_c} = 2\sqrt{\frac{d_1}{dt}} \int_0^r R \left(\frac{\partial c_1}{\partial X} \right)_{x=0} dR$$

Since the differential quotients $(\partial c_1/\partial X)$ are given at the collocation points we may calculate the integral exactly by a quadrature formula of the type (1, 26, p. 134)

$$(114) \quad \int_0^r f(r) w_j(r) dr = \sum_{i=1}^{n+1} Q_i f_i$$

where the Q_i are elements of a vector depending on the trial function chosen.

Thus, from (67)

$$(115) \quad \int_0^r R \left(\frac{\partial c_1}{\partial X} \right)_{x=0} dR = \sum_{i=1}^{n+1} Q_i \left[R_i A_{1,i+1} + R_i \sum_{j=1}^{n+1} A_{1,j} c_1(X_j, R_i, T) \right]$$

Expanding the sum over j and introducing the boundary conditions [36] and [42b], (115) changes to

$$(116) \quad \int_0^r R \left(\frac{\partial c_1}{\partial X} \right)_{x=0} dR = \sum_{i=1}^{n+1} Q_i \left[R_i A_{1,i+1} + R_i \sum_{j=1}^{n+1} A_{1,j} c_1(X_j, R_i, T) \right]$$

The Gaussian weights Q_i for $i=1$ and $i=N_o+2$ are equal to zero, thus (116) reduces to

$$(117) \quad \int_0^r R \left(\frac{\partial c_1}{\partial X} \right)_{x=0} dR = \sum_{i=1}^{n+1} Q_i \times \left[R_i A_{1,i+1} + R_i \sum_{j=1}^{n+1} A_{1,j} c_1(X_j, R_i, T) \right]$$

which is a convenient form for computation of the integral.

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Correlation of the hydrogenation catalytic activity of dinuclear complexes of rhodium(I) with the formation of carbonyl-bridged complexes

ALAN R. SANCHEZ

Alberta Research Council, 11113-87 Avenue, Edmonton, Alta., Canada T6G 2C7

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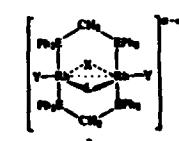
Méthodes sélectives de la catalyseur bimétallique de rhodium(I), $[Rh_2(\mu-X)CO_2(PPh_3)_6]_n^+$ ($X = Cl, Br; E = P, As$) et d'iridium(I), $[Ir_2(CO)_2(PPh_3)_6]_n^+$, sont deux catalyseurs actifs d'hydrogénéation des alcynes en alkenes et d'alcenes en alkans. On a également étudié les complexes neutres ayant des ligands pentadentatiques, mais trois complexes du type cyan ($[Rh_2(CN)_2(CO)_2(PPh_3)_6]_n^+$) et leurs analogues de type arsene ont une activité catalytique significative. Seuls les complexes qui forment un équilibre de manière réversible des complexes liés par un pont avec des ligands, tels le CO, sont également des catalyseurs actifs.

Les complexes stables avec des ligands diférents ne sont pas des catalyseurs efficaces dans les conditions étudiées.

(Traduit par le journal)

Introduction

The first dinuclear rhodium complex of the geometry designated "A-frame" (1) $[Rh_2(\mu-S)(Cu)(dpm)]$ (dpm is $PPh_3PPh_3PPh_3$ and sdm is $Ph_3AsCH_2AsPh_3$) was described in 1977 (1). The synthesis and structure of related complexes of rhodium or iridium has since received much attention (2-16). For complexes of rhodium(I), several instances of co-ordination of two-electron donor ligands (L ; e.g. CO, SO_2) at the site bridging the metal centers (2) have been reported (2, 3, 6, 9, 12-16). The complex cation, $[Rh_2(\mu-CIMCO)(dpm)]^+$, forms a 1:1 labile, symmetrical (irr^{13}P nmr) complex with diphenylacetylene (6),² and similar neutral complexes have also recently been described (11). Co-ordination of an alkyne at the bridging site (2; $L = \text{alkyne}$) is accompanied by lengthening of the carbon-carbon bond such that the product is accurately described as a *cis*-dimethylated alkynyl complex (11). No complex in which an alkyne is co-ordinated at either a bridging or terminal site of an A-frame complex has yet been described.



The A-frame structure, with the proximity of the two metal centres, has strong potential for di-nuclear activation of unsaturated substances. However, the complex $[Rh_2(\mu-S)CO_2(dpm)]$ has been shown to have low activity for the hydrogenation of ethylene (13). Herin I report that those cationic or neutral complexes of rhodium (or iridium) which form carbonyl-bridged complexes (2, $L = CO$) are more efficient.

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²This system has been investigated elsewhere (M. Cava, private communication) and in this laboratory. The differences in spectroscopic parameters between solutions of the complex and with the acetylene are now considered to be due to differences in conformation. A cationic complex containing $CH_3C\equiv CC\equiv CCO_2CH_3$ has been well characterized (11).

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